

PATENT SPECIFICATION

NO DRAWINGS

Inventor: FREDERICK HAROLD HOWELL

Date of filing Complete Specification: 23 Nov., 1967.

Date of Application (No. 52602/66): 21 Dec., 1966.

Complete Specification Published: 1 July, 1970.



Index at acceptance:—C2 C(3A10B2A, 3A10B5J, 3A10B5K)

In

ERRATA

SPECIFICATION No. 1,196,594

Page 1, line 33, for "3" read "5"
Page 1, line 57, for "and an" read "to and"
Page 2, line 27, for "indutrial" read "indus-
trial"

Page 4, line 50, for "ranges" read "range"
THE PATENT OFFICE
10th August 1970

pan
Sir
here
the
be p
ing s
T

10 process for the production of sebacic acid.

The hydrogenation of 5-ketosebacic acid in the form of the disodium salt to 5-hydroxysebacic acid and thence to sebacic acid itself has already been described by G. P. Chiusoli et al., Gazzetta Chimica Italia, 87, 90, 1957. These workers employed a Raney nickel catalyst and conducted the hydrogenation under pressure in two stages, firstly at 140°C., and subsequently at 270°C. However, the yield of sebacic acid achieved by this process was very poor, being of the order of 15%, the major product consisting of 5 - hydroxy - 1,10 - decanedioic acid - 1,5 - lactone.

We have now unexpectedly found that if the hydrogenation of 5-ketosebacic acid or 5-hydroxysebacic acid is effected in the presence of a palladium or platinum catalyst at a temperature above 200°C., almost quantitative yields of sebacic acid may be achieved.

According to the present invention, there is provided a process of producing sebacic acid comprising hydrogenating 5-ketosebacic acid or 3-hydroxysebacic acid or an alkali metal salt of either of said acids with molecular hydrogen at a temperature in excess of 200°C., and in the presence of a hydrogenation catalyst of palladium or platinum.

The hydrogenation reaction is preferably effected using the 5-ketosebacic acid or 5-hydroxysebacic acid in the form of an alkali metal salt, most preferably in the form of the disodium salt.

The hydrogenation is conveniently effected in solution, preferably aqueous solution, and

to sebacic acid of the 5-ketosebacic acid or 5-hydroxysebacic acid, or alkali metal salt of either acid, used as starting material, is achieved in the presence of a palladium or platinum hydrogenation catalyst at temperatures up to and including 200°C. Most surprisingly, however, if the hydrogenation temperature is raised relatively slightly to 225°C., excellent yields of sebacic acid may be obtained. The range of temperature which is most advantageously employed in the hydrogenation process of the invention has been found to be 225° to 275°C.

The hydrogenation is carried out in the presence of a palladium or platinum hydrogenation catalyst. The catalyst is conveniently supported on any of a variety of supporting media, for example, silica, alumina, asbestos, calcium carbonate, fuller's earth, pumice or other conventional catalyst carrier for platinum group metals; however, the preferred catalyst is palladium supported on charcoal or carbon black. The proportion of palladium or platinum metal present in the supported catalyst is advantageously within the range of from 1% to 10% by weight based on the total weight of the supported catalyst.

It is preferred that the hydrogenation reaction is conducted in the presence of an excess amount of molecular hydrogen over the stoichiometric proportion required for the conversion of the starting material to sebacic acid. The hydrogenation is advantageously carried out for a time period in excess of three hours, for instance for a time period within the range of from four to eight hours.

The 5-hydroxysebacic acid which may be

[Price 5s. 0d. (25p)]

SEE ERDATA SUP ATTACHED

BEST AVAILABLE COPY

PATENT SPECIFICATION

NO DRAWINGS

1.196.594



Inventor: FREDERICK HAROLD HOWELL

Date of filing Complete Specification: 23 Nov., 1967.

Date of Application (No. 52602/66): 21 Dec., 1966.

Complete Specification Published: 1 July, 1970.

Index at acceptance:—C2 C(3A10B2A, 3A10B5J, 3A10B5K)

International Classification:—O 07 c 55/20

COMPLETE SPECIFICATION

Improvements in and relating to the production of
Sebacic Acid

We, GEIGY (U.K.) LIMITED, a British Company, whose registered office address is Simonsway, Manchester 22, Lancashire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to an improved process for the production of sebacic acid.

The hydrogenation of 5-ketosebacic acid in the form of the disodium salt to 5-hydroxysebacic acid and thence to sebacic acid itself has already been described by G. P. Chiusoli et al., *Gazzetta Chimica Italia*, 87, 90, 1957. These workers employed a Raney nickel catalyst and conducted the hydrogenation under pressure in two stages, firstly at 140°C., and subsequently at 270°C. However, the yield of sebacic acid achieved by this process was very poor, being of the order of 15%, the major product consisting of 5-hydroxy-1,10-decanedioic acid - 1,5-lactone.

We have now unexpectedly found that if the hydrogenation of 5-ketosebacic acid or 5-hydroxysebacic acid is effected in the presence of a palladium or platinum catalyst at a temperature above 200°C., almost quantitative yields of sebacic acid may be achieved.

According to the present invention, there is provided a process of producing sebacic acid comprising hydrogenating 5-ketosebacic acid or 5-hydroxysebacic acid or an alkali metal salt of either of said acids with molecular hydrogen at a temperature in excess of 200°C., and in the presence of a hydrogenation catalyst of palladium or platinum.

The hydrogenation reaction is preferably effected using the 5-ketosebacic acid or 5-hydroxysebacic acid in the form of an alkali metal salt, most preferably in the form of the disodium salt.

The hydrogenation is conveniently effected in solution, preferably aqueous solution, and

under pressure in a suitable pressure reactor. The hydrogenation may be carried out at atmospheric or subatmospheric pressure, but the preferred pressure at which the hydrogenation procedure is effected is within the range of from 20 to 150 atmospheres.

It has been found that substantially no conversion to sebacic acid of the 5-ketosebacic acid or 5-hydroxysebacic acid, or alkali metal salt of either acid, used as starting material, is achieved in the presence of a palladium or platinum hydrogenation catalyst at temperatures up to and including 200°C. Most surprisingly, however, if the hydrogenation temperature is raised relatively slightly to 225°C., excellent yields of sebacic acid may be obtained. The range of temperature which is most advantageously employed in the hydrogenation process of the invention has been found to be 225° to 275°C.

The hydrogenation is carried out in the presence of a palladium or platinum hydrogenation catalyst. The catalyst is conveniently supported on any of a variety of supporting media, for example, silica, alumina, asbestos, calcium carbonate, fuller's earth, pumice or other conventional catalyst carrier for platinum group metals; however, the preferred catalyst is palladium supported on charcoal or carbon black. The proportion of palladium or platinum metal present in the supported catalyst is advantageously within the range of from 1% to 10% by weight based on the total weight of the supported catalyst.

It is preferred that the hydrogenation reaction is conducted in the presence of an excess amount of molecular hydrogen over the stoichiometric proportion required for the conversion of the starting material to sebacic acid. The hydrogenation is advantageously carried out for a time period in excess of three hours, for instance for a time period within the range of from four to eight hours.

The 5-hydroxysebacic acid which may be

employed as starting-material in the process of the present invention may be produced, for instance, by alkaline hydrolysis of 5-hydroxy - 1,10 - decanedioic acid-1,6-lactone according to the process which is described and claimed in our co-pending British patent application No. 21513/68 (Serial No. 1,196,596).

The 5-hydroxysebacic acid produced in this way is in the form of the di-alkali metal salt which is however readily converted into the free acid form by rendering the reaction mixture acidic, for instance with concentrated hydrochloric acid. By this means, the 5-hydroxysebacic acid may be precipitated from the reaction mixture and further purified, if desired, by conventional means such as fractional crystallisation.

The 5-ketosebacic acid which may also be employed as starting-material in the process of the present invention may be produced, for example, by oxidising cyclodec-5-enone according to the process described and claimed in our co-pending British patent application No. 21515/68 (Serial No. 1,196,598).

The sebacic acid produced according to the process of the present invention is an important industrial compound, especially in the form of its dialkyl esters. These esters find wide application both in the field of plasticisers for polyvinyl chloride and also as synthetic lubricants for modern turbo-jet aircraft engines.

The present invention is further illustrated by the following Examples. Parts by weight expressed therein bear the same relation to parts by volume as do kilograms to litres.

EXAMPLES 1 to 5

4.0 parts of 5-hydroxysebacic acid, 18.5 parts by volume of 1.90 N sodium hydroxide

solution and 2.0 parts of palladium catalyst supported on charcoal and containing 5% by weight of palladium, were placed in a 100 parts by volume capacity stainless steel autoclave which was mounted on a rocking device. The autoclave was purged with nitrogen and then pressurised to 115 atmospheres with hydrogen. The internal temperature of the autoclave was raised to 250°C., at which temperature the pressure increased to 165 atmospheres. Rocking of the autoclave was commenced and continued for 5 hours at 250°C. Afterwards the autoclave was allowed to cool to 25°C. and the pressure then decreased to 105 atmospheres.

The product was removed from the autoclave by washing out with hot water, the washings being filtered, concentrated to a small volume and acidified to a pH value of 4.0 with concentrated hydrochloric acid.

The white solid which separated was filtered off and dried to give 3.5 parts of sebacic acid having melting point 125° to 134°C., representing a yield of 95% theoretical. The product was examined by gas/liquid chromatographical methods and showed a sebacic acid content of 99.5% by weight.

Similar experiments were carried out under identical conditions except that the hydrogenation temperatures were varied. A further similar experiment was conducted under identical conditions but using a platinum catalyst supported on charcoal and 5% by weight of platinum, instead of the palladium catalyst. The results of these further experiments are shown in the following Table, which also includes for comparative purposes only data relating to an experiment carried out at 200°C.

TABLE

Example	Catalyst	Reaction temperature (°C)	Reaction time (hours)	Initial hydrogen pressure (atmospheres)	Acid value of product (mg./KOH/g)	Melting point of product °(C.)	Yield of sebacic acid (%)
—	Pd/C	200	5.5	68	515	100—102	—
1	Pd/C	225	6	94	542	130—132	81
2	Pd/C	250	5	115	521	125—134	95
3	Pd/C	250	6	94	532	128—134	92
4	Pd/C	275	6	117	538	131—133	87
5	Pt/C	250	6	110	531	127—129	76

EXAMPLE 6

3.0 parts of 5-ketosebacic acid, 12.7 parts by volume of 2.15 N sodium hydroxide solution, 7.3 parts by volume of water and 2.0 parts of palladium supported on charcoal containing 5% by weight of palladium were placed in a 100 parts by volume capacity stainless steel rocking autoclave. The autoclave was purged with nitrogen and pressurised to 110 atmospheres with hydrogen. The internal temperature of the autoclave was raised to 250°C., and held at this temperature for 17 hours. On cooling to 25°C., the pressure in the autoclave was 102 atmospheres.

The reaction product was removed from the autoclave by washing with water, filtering the washings, concentrating the washings to a small volume and acidifying the concentrate to a pH value of 4.0 with concentrated hydrochloric acid.

The white solid which precipitated was filtered off, washed with water and dried to give 2.3 parts of sebatic acid having a melting point of 130° to 133°C., and an acid value of 542 milligrams of potassium hydroxide per gram, representing a yield of 82% theoretical.

WHAT WE CLAIM IS:—

1. A process of producing sebatic acid comprising hydrogenating 5-ketosebacic acid or 5-hydroxysebatic acid or an alkali metal salt of either of said acids with molecular hydrogen at a temperature in excess of 200°C., and in the presence of a hydrogenation catalyst of palladium or platinum.

2. A process as claimed in claim 1 wherein a disodium salt of 5-ketosebacic acid or 5-hydroxysebatic acid is employed as starting-material.

3. A process as claimed in either claim 1 or claim 2 wherein the hydrogenation is effected in solution.

4. A process as claimed in claim 3 wherein the hydrogenation is effected in aqueous solution.

5. A process as claimed in any of the previous claims wherein the hydrogenation is effected at a superatmospheric pressure.

6. A process as claimed in claim 5 wherein the hydrogenation is effected at a superatmospheric pressure within the ranges of from 20 to 150 atmospheres.

7. A process as claimed in any of the preceding claims wherein the hydrogenation is effected at a temperature within the range of from 225° to 275°C.

8. A process as claimed in any of the preceding claims wherein the catalyst is supported on silica, alumina, asbestos, calcium carbonate, fuller's earth or pumice.

9. A process as claimed in any of claims 1 to 7 wherein the catalyst is palladium supported on charcoal or carbon black.

10. A process as claimed in claim 8 or 9 wherein the proportion of palladium or platinum metal in the supported catalyst is within the range of from 1% to 10% by weight based on the total weight of the supported catalyst.

11. A process as claimed in any of the preceding claims wherein the hydrogenation is effected using an excess amount of molecular hydrogen over the stoichiometric proportion required for the conversion of the starting-material to sebatic acid.

12. A process as claimed in any of the preceding claims wherein the hydrogenation is carried out for a time period in excess of three hours.

13. A process as claimed in claim 12 wherein the time period is within the range of from four to eight hours.

14. A process of producing sebatic acid substantially as described in any of Examples 1 to 6.

15. Sebatic acid whenever produced by a process claimed in any of the preceding claims.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1.
Chartered Patent Agents.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.